

Fulde-Ferrell-Larkin-Ovchinnikov State and Field-Induced Superconductivity in an Organic Superconductor

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An experimental phase diagram of the field-induced superconductivity in the λ -(BETS)₂FeCl₄ compound is theoretically reproduced by a combination of the Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) state and the Jaccarino-Peter mechanism. Semi-quantitative agreement is obtained in the presence of a very weak subdominant triplet pairing interaction between electrons with antiparallel spins, in addition to a dominant singlet pairing interaction. An order-parameter mixing effect enhances the FFLO state and plays an essential role in the semiquantitative agreement. As a possible origin of the small triplet component, pairing interactions mediated by spin fluctuations are proposed. It is argued that, in this mechanism of the pairing interactions, equal spin pairing interactions are much weaker than the antiparallel spin pairing interactions in the strong magnetic field, which is consistent with the lack of observation of equal spin state.

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Recently, a field-induced superconductivity (FISC) was observed at high magnetic fields in an organic superconductor λ -(BETS)₂FeCl₄, (BETS = bis-(ethylenedithio)tetraselenafulvalene) [1]. The lower critical field $H_c^{\text{low}}(T)$ of the FISC is upwards convex [2,3] as a function of temperature T . When we consider the Jaccarino-Peter mechanism [4] as the origin of the FISC [2,5,6], the lower critical field corresponds to the upper critical field of a typical superconducting phase. Therefore, the upwards convex $H_c^{\text{low}}(T)$ is not a common characteristic of the upper critical field. Some authors argued [2,3,5] that this upturn behavior can be explained by the Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) state [7–12].

The FFLO state has been discussed in some other organic superconductors, because some of them satisfy the necessary conditions for the FFLO state to occur: (1) Those samples can be clean type II superconductors due to their narrow electron bands; (2) The orbital pair-breaking effect is strongly suppressed for parallel magnetic fields due to the low dimensionality. The present compound λ -(BETS)₂FeCl₄ also exhibits these features.

The upturn due to the FFLO state in the cylindrically symmetric system was obtained by Bulaevskii [9] and Aoi et al. [10]. The FFLO state in two-dimensional superconductors was reexamined and discussed in connection with exotic superconductors, such as organics and cuprates, by some authors [11–19]. The upturn is a common behavior of the FFLO state in quasi-two-dimensional systems [13–19]. This behavior is due to a Fermi surface effect [11,13,14] analogous to Fermi surface nesting for the spin-density and charge-density waves, which we call a nesting effect for the FFLO state.

On the other hand, an upturn of the upper critical field ($d^2H_c/dT^2 > 0$) and a first-order transition below the upper critical field have been observed in κ -(BEDT-TTF)₂Cu(NCS)₂ [20–23]. The FFLO state has also been discussed in this compound. Manalo and Klein [24] have successfully confirmed the agreement between the exper-

imental [20–22] and theoretical results [17].

A recent experiment on thermal conductivity by Tanatar et al. [25] supports the existence of the FFLO state in λ -(BETS)₂GaCl₄. They observed that the upper critical field is consistent with the Pauli paramagnetic limit in dirty samples, while it shows no saturation down to 0.3 K in clean samples. This experimental result supports the FFLO state also in the FISC in λ -(BETS)₂FeCl₄, since these two compounds are similar, except λ -(BETS)₂FeCl₄ has the magnetic anions.

In λ -(BETS)₂FeCl₄, localized spins of $S = 5/2$ on the $(\text{FeCl}_4)^{-1}$ anions create an exchange field on the conducting layer of the two-dimensional network of BETS molecules. As many authors pointed out [1,2,5,6], the exchange field shifts the Zeeman energy effectively, and thus also the superconductivity area in the B - T phase diagram. This compensation mechanism is called the Jaccarino-Peter mechanism, which was originally proposed for the FISC in ferromagnetic metals. The present compound is an antiferromagnetic insulator at zero field, but this difference does not affect the mechanism at high magnetic fields, where the localized magnetic moments are saturated [2,5,6].

Balicas et al. have compared the experimental phase diagram of λ -(BETS)₂FeCl₄ with the theoretical one with the FFLO state, taking into account the shift of the FISC area by the Jaccarino-Peter mechanism [2]. The main features of the FISC have been reproduced qualitatively by a combination of the FFLO state and the Jaccarino-Peter mechanism.

However, from a quantitative viewpoint, the theoretical width of the magnetic field region of the FISC is much narrower than the experimental one. In the experimental phase diagram, the FISC area has a center at about 33 T and the lower limit at about 17 T [3], which means that the absolute value of the critical field is equal to about 16 T in the absence of the exchange field. When the orbital pair breaking effect is ignored, the maximum transition temperature $T_c^{(m)} \approx 4.2$ K gives

the Pauli paramagnetic limit $1.856[\text{T/K}] \times T_c^{(\text{m})} = 7.8 \text{ T}$ and the s -wave FFLO critical field 11 T for the cylindrical Fermi surface. Therefore, the experimental value 16 T is much larger than the estimates using the simple theory.

Therefore, we need an explanation for this difference. There are some mechanisms which enhance the FFLO critical field, such as the effects of the anisotropies of the Fermi surface and the gap function [13–18]. In particular, by a nesting effect, the critical field can be enhanced up to a value several times as large as the Pauli paramagnetic limit [13,14]. However, the increase due to this mechanism occurs at low temperatures [15], and the tricritical point does not change. In the case of λ -(BETS) $_2$ FeCl $_4$, it seems that the shape of the FISC area in the experimental phase diagram is not reproduced very well solely by these mechanisms.

Another mechanism is an order-parameter mixing effect. In the presence of a subdominant triplet pairing interaction between electrons with antiparallel spins, even if it is very weak, the upper critical field is largely enhanced. This effect was theoretically predicted in s -wave superconductors with a spherical symmetric Fermi surface [26], and also in s - and d -wave superconductors with quasi-two-dimensional Fermi surfaces [19]. In the latter study, this effect was discussed in connection with the organic superconductors. Subdominant triplet pairing components exist in the pairing interactions mediated by the spin fluctuations [27,28], and also in those mediated by phonons [29]. In the latter, the triplet pairing component is enhanced due to the weakness of the screening effect in the low dimensions [30].

In this paper, we reproduce a phase diagram that agrees with the experimental data semiquantitatively, by taking into account the order-parameter mixing effect in the FFLO state with the Jaccarino-Peter mechanism.

Before we analyze of the FISC, let us briefly discuss the exchange field created by the $(\text{FeCl}_4)^{-1}$ anions. In our previous paper [5], we proposed a mechanism which enhances the upper critical field in antiferromagnetic superconductors. In order to illustrate the mechanism, we used a generalized Kondo lattice model of the localized spins and mobile electrons with a Kondo coupling J_K between them and an antiferromagnetic exchange coupling J between the localized spins. As a special case, the model describes an aspect of the λ -(BETS) $_2$ FeCl $_4$ compound, for a half-filled electron band and large ratios of J_K/zJ , where z is the number of the nearest neighbor sites. In the application to the λ -(BETS) $_2$ FeCl $_4$ compound, J should be replaced with some indirect interaction via conducting layers [6,31], which must be much smaller than J_K . Therefore, it is expected that the ratio J_K/zJ is much smaller than 1. The RKKY exchange interaction and the reconstructed Fermi surface have been calculated by Brossard et al. [31].

In the calculation based on the generalized Kondo lattice model [5], the boundary between the antiferro-

magnetic insulating phase and the paramagnetic metallic phase is $B_{\text{MI}} = \mu_0 H_{\text{MI}} = \mu_0 zJS/|\mu_e|$, where μ_0 is the magnetic permeability and μ_e is the electron magnetic moment. On the other hand, the compensation effect shifts the center of the FISC area by

$$B_{\text{cent}} = \mu_0 H_{\text{cent}} = \mu_0 \frac{J_K S}{|\mu_e|}. \quad (1)$$

Therefore, from the experimental data [1], $B_{\text{MI}} \approx 10.5 \text{ T}$ and $B_{\text{cent}} \approx 33 \text{ T}$, we obtain the ratio

$$\frac{J_K}{zJ} = \frac{B_{\text{cent}}}{B_{\text{MI}}} \approx 3.1 \gg 1, \quad (2)$$

which is consistent with the above consideration.

From the values $B_{\text{cent}} = 33 \text{ T}$, $B_{\text{MI}} = 10.5 \text{ T}$ and $S = 5/2$, we obtain $J_K/k_B \approx 8.87 \text{ K}$ and $zJ/k_B = 2.82 \text{ K}$. The mean field value of the antiferromagnetic transition temperature $T_{\text{AF}}^{\text{MF}}$ is equal to $zJS(S+1)/4 \approx 8.1 \text{ K}$, which agrees very well with the experimental value 8.5 K .

Now, let us examine the FISC. We examine the case in which a dominant singlet pairing interaction and a very weak subdominant triplet pairing interaction coexist between electrons with antiparallel spins. The pairing interaction and the gap function are expanded as

$$\begin{aligned} V(\mathbf{k}, \mathbf{k}') &= - \sum_{\alpha} g_{\alpha} \gamma_{\alpha}(\mathbf{k}) \gamma_{\alpha}(\mathbf{k}'), \\ \Delta(\mathbf{k}) &= \sum_{\alpha} \Delta_{\alpha} \gamma_{\alpha}(\mathbf{k}), \end{aligned} \quad (3)$$

with symmetry factors $\gamma_{\alpha}(\mathbf{k})$. In cylindrically symmetric systems, they are defined by, for example, $\gamma_s(\mathbf{k}) \propto 1$, $\gamma_{p_x}(\mathbf{k}) \propto \hat{k}_x$, $\gamma_{d_{x^2-y^2}}(\mathbf{k}) \propto \hat{k}_x^2 - \hat{k}_y^2$, and so on. We normalize $\gamma_{\alpha}(\mathbf{k})$ by

$$\int_0^{2\pi} \frac{d\varphi}{2\pi} [\gamma_{\alpha}(\varphi)]^2 = 1, \quad (4)$$

where $\gamma_{\alpha}(\varphi) = [\gamma_{\alpha}(\mathbf{k})]_{|\mathbf{k}|=k_F}$ and φ is the angle between \mathbf{k} and k_x -axis. We assume a cylindrically symmetric Fermi surface for simplicity, and s -wave and p -wave pairing interactions as the dominant and subdominant pairing interactions, respectively [34]. Later, we will discuss the effects of the anisotropies of the Fermi surface and the gap function.

In the weak coupling limit, the gap equations are written as

$$\Delta_{\alpha} \log \frac{T}{T_{c\alpha}^{(0)}} = - \sum_{\beta} M_{\alpha\beta} \Delta_{\beta}, \quad (5)$$

where we define

$$\begin{aligned} M_{\alpha\beta} &\equiv \int_0^{2\pi} \frac{d\varphi}{2\pi} \gamma_{\alpha}(\varphi) \gamma_{\beta}(\varphi) \sinh^2 \frac{\beta\zeta}{2} \Phi(\varphi), \\ \Phi(\varphi) &\equiv \int_0^{\infty} dy \frac{\tanh y}{y (\cosh^2 y + \sinh^2 \frac{\beta\zeta}{2})}, \end{aligned} \quad (6)$$

$$T_{c\alpha}^{(0)} = 2e^{\gamma} \pi^{-1} \omega_c e^{-1/g_{\alpha} N(0)},$$

with $\zeta = h [\bar{q} \cos(\varphi - \varphi_{\mathbf{q}}) + 1]$, $\bar{q} = v_F q / 2h$, $h = |\mu_e|(|H| - H_{\text{cent}})$, $N(0)$ the density of states at the Fermi energy, and $\varphi_{\mathbf{q}}$ the angle between the center-of-mass momentum \mathbf{q} of the FFLO state and the k_x -axis.

For the symmetry, we can assume the direction of \mathbf{q} along the k_x -axis without loosing generality. Then, the p_y -wave component $\Delta_{p_y} \hat{k}_y$ is not mixed with the s -wave component, while the p_x -wave component $\Delta_{p_x} \hat{k}_x$ is mixed with it. Therefore, the transition temperature for a given \mathbf{q} is calculated by $T_c(h, \mathbf{q}) = T_{cs}^{(0)} e^{-\lambda(h, \mathbf{q})}$ with the smallest eigenvalue $\lambda(h, \mathbf{q})$ of the 2×2 matrix

$$\begin{pmatrix} M_{ss} & M_{sp} \\ M_{ps} & M_{pp} + G_p \end{pmatrix}, \quad (7)$$

where we define

$$G_p \equiv \log \frac{T_{cs}^{(0)}}{T_{cp}^{(0)}} = \frac{1}{g_p N(0)} - \frac{1}{g_s N(0)}. \quad (8)$$

Here, $T_{cs}^{(0)}$ and $T_{cp}^{(0)}$ are the pure s - and p -wave transition temperatures. In the presence of the exchange field, $T_{cs}^{(0)}$ is equal to the maximum transition temperature $T_c^{(m)}$ of the FISC. The final result of the transition temperature is obtained by maximizing $T_c(h, \mathbf{q})$ with respect to \mathbf{q} .

The results are depicted in Fig. 1. The FFLO critical fields are largely enhanced even for a very small value of the coupling constant of the coexisting triplet pairing interaction. Figure 1(a) shows the result for $T_c^{(m)} = 4.2$ K and $T_{cp}^{(0)} = 0.084$ K, which corresponds to $T_{cp}^{(0)}/T_c^{(m)} = 1/50$ and $G_p \approx 3.912$. It is found that the agreement between theoretical and experimental results is significantly improved by taking into account the weak triplet pairing interaction (solid curve), in comparison to the result in the absence of the triplet pairing interactions (dotted curve). Taking into account the ambiguity in determination of the experimental values of the transition temperatures [1–3], it can be concluded that the overall behavior of the transition curve is semiquantitatively reproduced by the FFLO state.

Figure 1(b) is the result for $T_c^{(m)} = 4.5$ K and $T_{cp}^{(0)} = 0.045$ K, which corresponds to $T_{cp}^{(0)}/T_c^{(m)} = 1/100$ and $G_p \approx 4.605$. Except near the top of the peak, the theoretical curve agrees very well with the experimental data.

In the above calculations, the presence of the weak triplet pairing interactions between electrons with antiparallel spins is assumed. When the system is isotropic in the spin space, triplet pairing interactions between electrons with parallel spins are of the same magnitude at zero field. In this case, one might expect transitions to an equal spin pairing state at magnetic fields where the FISC of antiparallel spin pairing is suppressed. For example, in the cases shown in Figs. 1(a) and 1(b), the transition temperatures of the equal spin state are equal to 84 mK and 45 mK, respectively. However, such transitions have not been observed in the experiments.

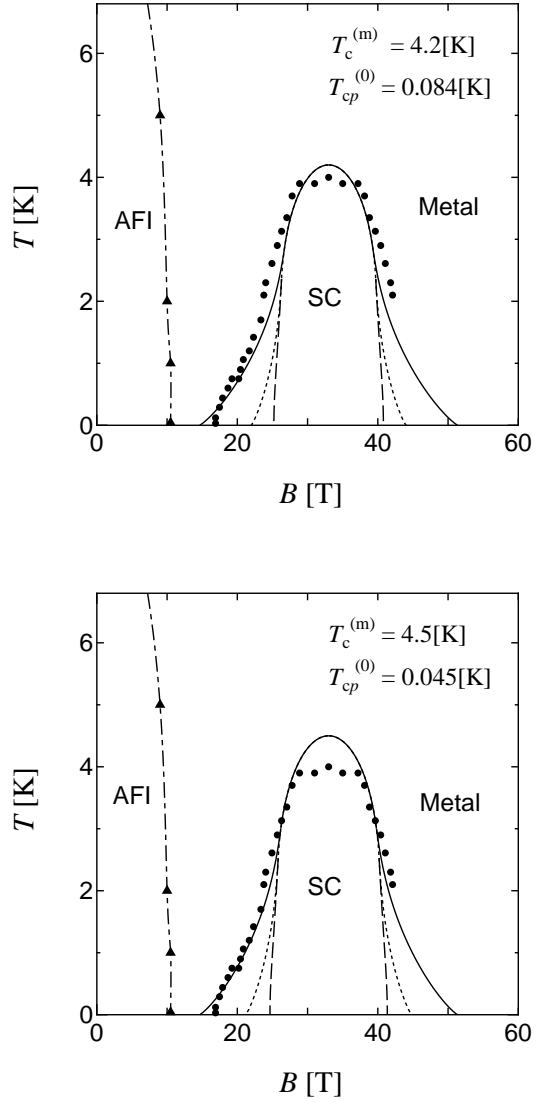


FIG. 1. Comparison between the theoretical and experimental phase diagrams in λ -(BETS) $_2$ FeCl $_4$. We set the maximum value of the superconducting transition temperature (a) $T_c^{(m)} = 4.2$ K and $T_{cp}^{(0)} = 0.084$ K, and (b) $T_c^{(m)} = 4.5$ K and $T_{cp}^{(0)} = 0.045$ K. The strength of the exchange field is assumed so that the center of the peak B_{cent} is equal to 33 T. The solid, dotted, and dashed curves show boundaries of the FISC, in the presence of the triplet pairing interaction, in the absence of it, and when the FFLO state is excluded, respectively. The solid circles and the solid triangles show the experimental data of the superconducting and antiferromagnetic transition points, respectively, by Uji et al. in ref. [3]. The dot-dashed curve is a guide for the eyes.

This discrepancy can be explained if the origin of the triplet pairing interactions is the exchange of the spin fluctuations enhanced by on-site Coulomb repulsion [27,32]. For example, in a random phase approximation (RPA), the equal spin pairing interactions originate from the fluctuations as shown in the diagrams in Fig. 2(a) [27]. Therefore, they correspond to the fluc-

tuations of S_z components. On the other hand, the antiparallel spin pairing interactions originate from the fluctuations as shown in the diagrams in Figs. 2(b) and 2(c) [27,32] in the RPA. They correspond to the fluctuations of S_z components and $S_{\pm} \equiv S_x \pm iS_y$, respectively. In the magnetic field in the z -direction, since the spin moment $\langle S_z \rangle$ is finite, the spin fluctuations of z components are much smaller than those of x and y components. Therefore, the equal spin pairing interactions are much weaker than the antiparallel spin pairing interactions in the magnetic field.

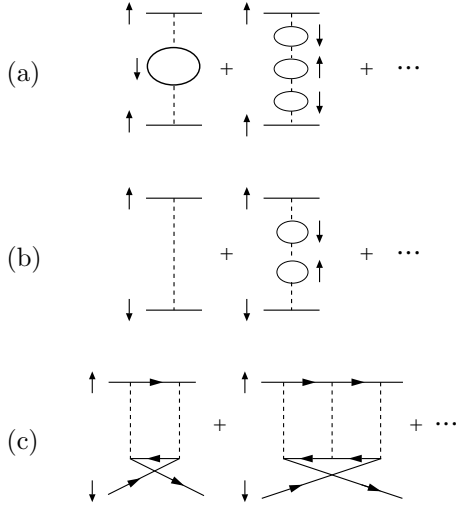


FIG. 2. Series of diagrams of fluctuations which contribute to the pairing interactions. The short dashed line denotes the on-site Coulomb interaction U .

Another possible explanation is the orbital pair-breaking effect. The transition temperature of the equal spin pairing state is only 45 mK in the case shown in Fig. 1(b). If we take into account the orbital pair-breaking effect, the equal spin pairing state with such a small transition temperature may be suppressed completely at higher magnetic fields where the system is metallic.

In this paper, we have assumed the s -wave pairing interaction as the dominant singlet interaction, and the cylindrical Fermi surface for simplicity [34]. For the d -wave pairing, the curve of the critical field exhibits a kink at a low temperature [16–18]. However, the kink disappears when the Fermi surface is anisotropic to some extent [15]. Furthermore, the anisotropy of the Fermi surface enhances the critical field [13,14] for a nesting effect. However, since the enhancement occurs especially at low temperatures $T \lesssim 0.2T_c$ [15], the mixing effect remains necessary for the semiquantitative reproduction of the experimental phase diagram in an entire temperature region including $T \gtrsim 0.2T_c$.

In conclusion, the phase diagram of λ -(BETS) $_2$ FeCl $_4$ including the curve of the lower limit of the FISC which is

upwards convex ($d^2H_c(T)/dT^2 < 0$) can be explained by the combination of the FFLO state and the Jaccarino-Peter mechanism, together with the order-parameter mixing effect. For the semiquantitative reproduction of the phase diagram in the present theory, the existence of the very weak subdominant triplet pairing interaction is essential. The origin of it can be attributed to spin fluctuations in the magnetic field. The phase diagrams of λ -(BETS) $_2$ Ga $_{1-x}$ Fe $_x$ Cl $_4$ are also expected to be understood in the present mechanism. The experimental evidence of the existence or inexistence of the FFLO state can be obtained by direct observations of the structure of the gap function [33,35].

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